RHEOLOGICAL CHARACTERIZATION OF THERMOSETTING RESIN SYSTEM WITH THERMOPOLYMER FUNCTIONAL LAYER

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ABSTRACT

Broader application of fibre reinforced plastics leads to more challenges, in term of the complexity of the parts design and more in the materials combination. Combining polymer matrices, such as thermosetting and thermoplastic polymers, will result in parts with advantages of properties from both polymers. The bonding strength of the combined polymers is depending on the diffusion of thermoplastic and thermosetting polymers, the so called SIPN (semi interpenetrated network) at the interface between the two polymers. It is therefore important to characterize and to understand the formation and the development of the SIPN layer. Rheological approach is proposed for the characterization of the SIPN layer.

This Study addresses the preparation of the layered thermoplastic thermosetting samples for the oscillatory viscosity measurement and the measuring procedures for the SIPN characterization. The development of SIPN layer in the layered thermoplastic thermosetting sample causes a viscosity change overtime. By applying this measuring method important information such as which component of the resin system is responsible for the formation of the SIPN, the development of SIPN layer in dependency of curing time and temperature can be determined.

1 INTRODUCTION

The increasing percentage of structural parts made of fibre reinforced plastics, for example in aircraft and automotive industries, also means increasing complexity in the parts design, which leads to more differential parts construction and bonding process is therefore inevitable. While thermoplastic fibre reinforced plastics can be welded together, thermosetting fibre reinforced plastics on the other hand, due to its chemical structure, are not weldable and therefore only non-thermal bonding process such as riveting and adhesive bonding can be applied. Some Problems that can occur by riveting of fibre reinforced plastics are notch effect and additional weight from the rivets and sealing compound. Adhesive bonding is relatively time consuming, since its bonding quality is highly dependent on the surface treatment and the curing process of the adhesive material.

An alternative solution to bond thermosetting fibre reinforced plastics is by applying thermoplastic functional layer on the surface of the joining parts. Due to the nature of the thermoset, the application of the thermoplastic functional layer must take place in-situ during the manufacturing of the thermosetting fibre reinforced plastics parts. An interaction between thermosetting resin and thermoplastic layer occurs during the curing process and it develop a so called SIPN (semi interpenetrated networks) on the thermoset thermoplastic interface [1]. Unlike adhesive bonding, where its bonding interface shows a sudden material change, the SIPN layer on the thermoset thermoplastic interface builds a seamless material transition, which also means a better transmission of forces in the joined parts.

The application of thermoplastic functional layer on thermosetting fibre reinforced parts and the resulting bonding strength require fully understanding of the formation and development of SIPN layer. The characterization of the SIPN layer delivers important information such as which component of the
resin system is responsible for the formation of the SIPN, the development of SIPN layer in dependency of curing time and temperature and respectively the mechanical properties of the SIPN layer.

There are several common analytical methods that can be used to characterize the SIPN layer. Scanning Electron Microscopy (SEM) delivers the micrographic images of the SIPN zone (Figure 1) and the thermoset thermoplastic ratio or gradient in the SIPN layer can be determined through the element distribution resulted from Energy-dispersive X-ray spectroscopy (EDX) (Figure 2) [2,3]. Both methods can be used to determine the momentary state of the SIPN layer but not the development over time of the SIPN zone. For the latter purpose, it is necessary to find another analytical method that less cost intensive and less time consuming in the preparation and applicable to various thermoset thermoplastic combinations.

Figure 1: Scanning Electron Microscopy (SEM) images of fracture surface of SIPN layer between thermoplastic (PEI) and thermosetting (epoxy resin) polymers [2]

Based on the fact, that the thermoplastic thermosetting blend shows a different rheological behaviour than the individual polymer, the use rheological approach to characterize the SIPN layer is therefore feasible. Rheological measurement of thermoplastic thermosetting polymer blend has been investigated before, with the focus of the investigation on the determination of the influence of the thermoplastic polymer on the curing process of the thermoset [4]. The common rheological measurement setup and procedures, which are intended only for measurement using bulk thermoplastic thermosetting polymer blend, are not applicable for investigation of the formation and development of SIPN layer on the thermoset thermoplastic interface.

Figure 2: Determination of thermoplastic (PEI, PES) and thermoset (epoxy resin) distribution in SIPN layer using Energy-dispersive X-ray spectroscopy (EDX) [2]
The characterization approach suggested in this work utilizes the effect of the time-related change of the material composition, due to formation of SIPN layer on the thermoset thermoplastic interface, on the viscosity value to indirectly detect the formation and development of SIPN layer in the interface between the thermoplastic layer and thermosetting resin during the curing process. For this purpose, modification of the measuring geometry/plate is necessary and it is important to choose the right measuring parameters such as measuring gap, frequency and strain, to get visible and significant time-related viscosity changes due to the formation and development of the SIPN layer.

2  MEASURING PRINCIPAL AND PARAMETERS

2.1 Measuring Principal

The measurement principal for the characterization of the SIPN layer is based on the change of viscosity value, due to the change of measuring gap during the experiment. At the beginning of the measurement, there is a definite phase boundary or interface between thermoplastic foil in solid state and thermosetting resin in viscous liquid state. In the course of time, the liquid thermosetting resin diffuses into the thermoplastic and an SIPN is formed. Since the newly formed thermoplastic and thermosetting blend on the interface is viscous, there is a shift in the position of solid-viscous interface, which also means the change of the measuring gap. The change of measuring gap will influence the viscosity value.

2.2 Instrument setup and measuring parameters

The characterization of SIPN layer in this study were conducted using AR2000 Rheometer from TA Instruments with parallel plate setup and oscillation measuring mode. Disposable aluminium plate in 25 mm diameter is being used as upper measuring plate. Peltier plate is used as the lower measuring plate, allowing direct active tempering of the resin sample throughout the experiment. Isolation chamber is used to ensure controlled environment surrounding the measuring plate and the sample.

As already mentioned, modification of the upper measuring plate is necessary. Thermoplastic sample in foil form is attached using epoxy adhesive to the upper measuring plate, which allow the foil to oscillate together with the upper plate.
Figure 5: Rheometer with parallel plate setup for the characterization of SIPN layer

Figure 6: Rheometer sample for the characterization of SIPN layer

Oscillation measuring mode is chosen, since reactive thermosetting resin is involved and the measurement last until the resin is fully cured. For the characterization of the SIPN layer, the optimum or range of measuring parameters such as measuring gap, oscillation frequency and oscillation displacement, or respectively, strain must first be determined to get visible and significant viscosity changes in conjunction with the development of the SIPN layer. Preliminary parameters study has shown, that following measuring parameters values will give significant viscosity change during the measurement: 200 µm initial geometry gap, oscillation at 50 Hz frequency and 0.1% strain.

4 EXPERIMENTAL

4.1 Material

For the purpose of this study 0.125 mm polyetherimide (PEI) foil, Tecfilm TC00420 PEI, from Dr. D. Müller Ahlhorn GmbH is used. As for the thermosetting polymer two components epoxy resin system HexFlow RTM6-2 from Hexcel is chosen. The resin system consist of epoxy resin part, Tetruglycidyl Methylenediamine (TGMDA), and hardener part, a mixture of 4,4ʼ-Methylenebis(2,6-diethylenamine) (MDEA) and 4,4ʼ-Methylenebis(2-Isopropyl-6-methylenilane) (M-MIPA).

4.2 Measuring Procedures

At first, to determine which component of the epoxy resin system responsible for the development of SIPN and the influence of the temperature on the development of SIPN, rheological measurements with different material pairs (resin-thermoplastic foils and hardener-thermoplastic foils) were conducted at various isothermal temperatures (120°, 140°C, 160°C and 180°C). Further rheological measurement with epoxy resin mixture and thermoplastic foil were conducted also at various isotheal curing temperatures (120°, 140°C, 160°C and 180°C). For reference values, the same procedures were applied in the measurements of only epoxy resin samples (without thermoplastic foil).

After each experiment, the disposable aluminium plate with thermoplastic foil and cured sample is cut and prepared for microscopic analysis of the cross-section of the sample. By etching the surface of the microscope samples using dichloromethane solution clear phase boundaries between thermoplastic foil, epoxy resin layer and the SIPN layer can be seen on the surface of the sample (Figure 7). The etched sample is observed under light microscope to visually determine the thickness of the SIPN-layer.
5 RESULTS AND DISCUSSIONS

5.1 Solubility of thermoplastic foil in epoxy resin components

The results of the oscillatory viscosity measurement of epoxy resin components and thermoplastic foils can be seen in Figure 8. The experiments involving only the epoxy resin component (TGMDA) show an increase of viscosity over time starting from 140°C (Figure 8, right side). Since there was no hardener involved in these measurements the curing reaction can be excluded. Therefore, the increase of viscosity indicates, that PEI is soluble in epoxy resin component. Similar experiments with hardeners show an opposite result, since no viscosity change is seen in the graph. This means that the foil is not solved by the hardener (MDEA + M-MIPA).

![Solubility of Polyetherimide (PEI) and RTM6-2 components](image)

Figure 8: Solubility of polyetherimide (PEI) and RTM6-2 components (epoxy resin and hardener)

5.2 Development of SIPN layer at different curing temperatures

The next step in the rheological analysis of SIPN is the development of SIPN during the curing process of the epoxy resin mixture. An example of the rheological measurement result of PEI and epoxy resin sample until fully cured state can be seen in Figure 9. The liquid-solid phase change (gel point) of the epoxy resin sample will be defined as the intersection of the storage modulus (G’) and the loss modulus (G”).

![Development of SIPN layer](image)

As already mentioned in the procedure, a reference viscosity curve was made by using only epoxy resin sample. By comparing both viscosity curves, between PEI-epoxy resin and only epoxy resin at the same measuring temperature, it can be seen, whether there is a viscosity change or not. Since the only difference of the samples is the presence of thermoplastic foil, the viscosity change is due to the build-up of SIPN on the PEI-epoxy resin interface. The example of the comparison of viscosity curves can be seen in Figure 10.
Figure 9: Result of the rheological measurement of RTM6-2 + PEI foil until fully cured state

From the full-scale viscosity curve as shown in Figure 9, the focus of the analysis will be the area below the gel point respectively gel time (Figure 10).

Figure 10: Comparison of the viscosity curves (reference and PEI-epoxy resin) and its description regarding to the development of the SIPN.
As shown in Figure 10-A, from the reference curve, it is known that at the beginning of the measurement no significant viscosity change due to resin curing reaction can be seen. This can also be seen on the course of viscosity curve from PEI-epoxy resin sample that resembles the course of reference (epoxy resin) curve at the beginning of the measurement. After a certain curing time, a significant increase of viscosity can be seen on the PEI-epoxy resin sample. The deviation point will be defined as the beginning of the SIPN.

The deviation of the viscosity curve continues further as the curing advances (Figure 10-B). In this time range, the increase of viscosity in the PEI-epoxy resin sample is caused by the curing reaction and the development of SIPN layer. In Figure 10-C, it can be seen, that close to the gel point the course of viscosity curve from PEI-epoxy resin sample will once again resembles the course of the reference curve. The time where both curves show the same course again will be defined as the end of the SIPN development. After this time, up to the gel point, the significant viscosity change is caused only by the curing of the epoxy resin.

The viscosity change and the thickness of the SIPN layer can be corresponded by conducting the microscopic analysis on the cured PEI-epoxy resin sample. The microscopic analysis shows, as expected, that an SIPN layer was formed on the interface area between the thermoplastic foil and epoxy resin sample.

![Microscopic images of cross-sectional area from the rheometer samples: PEI-epoxy resin mixture and PEI foil at different curing temperatures](image)

The microscopic images of the SIPN layer in epoxy resin/PEI samples at different curing temperatures can be seen in Figure 11. The microscopic images show that at 120°C and 140°C isothermal curing condition, no SIPN layer is developed on the PEI-epoxy resin interface. SIPN-layer can be seen on samples at 160°C and 180°C isothermal curing condition. These results are corresponded to the results of the viscosity measurements: At 120°C and 140°C no deviation of the viscosity curves can be seen, since no SIPN was formed on the interface. On the other hand, curve deviation can be seen on samples at 160°C and 180°C curing temperatures. The summary of the results from the rheological analysis of the SIPN development in PEI-epoxy resin samples can be seen in Table 1.

<table>
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<tr>
<th>Isothermal curing Temperature (°C)</th>
<th>Gel time (min.)</th>
<th>Beginning of SIPN Formation (min.)</th>
<th>End of SIPN Formation (min.)</th>
<th>Length of SIPN Development (min.)</th>
<th>Thickness of SIPN layer (µm)</th>
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<td>10.4</td>
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</table>

Table 1: Summary of the rheological analysis of SIPN development in PEI-epoxy resin samples

6 CONCLUSIONS

The results of the study presented in this paper have shown, that by special preparation of the sample for plate-plate rheometer, it is possible to characterize the SIPN development between thermoplastic foil (PEI foil) and epoxy resin (RTM6-2) using rheological approach during the curing process.
In combination with microscopic analysis the correlation between viscosity change during rheological measurement and the SIPN thickness in the sample can be made. In case of SIPN layer formation between PEI and RTM6-2 in isothermal curing condition, the result of the study shown that no SIPN layer is formed at curing temperatures below around 160°C. The thickness of the SIPN layer is between 54 µm to 76 µm at 160°C and 180°C isothermal curing temperature respectively.

The next step following this study will be the analysis of the above gel point area to determine the mechanical properties of the SIPN layer. Further developments on this rheological measuring method of SIPN development are necessary to get a better measurement result. Especially, the optimum measuring gap must be found to get a significant viscosity change to the reference viscosity curve. Further experiments must be done to see if this method also applicable for other thermoplastic foils and resin systems.

REFERENCES


